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AMERICAN LEATHER CHEMISTS ASSOCIATION

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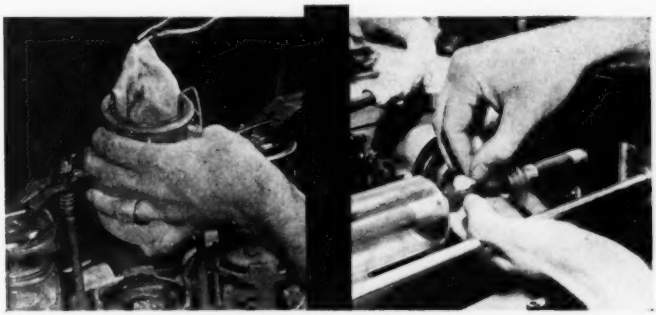

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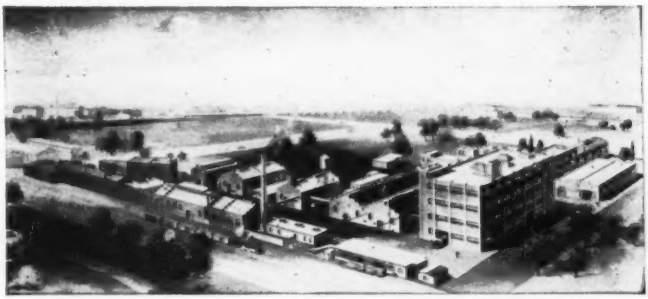

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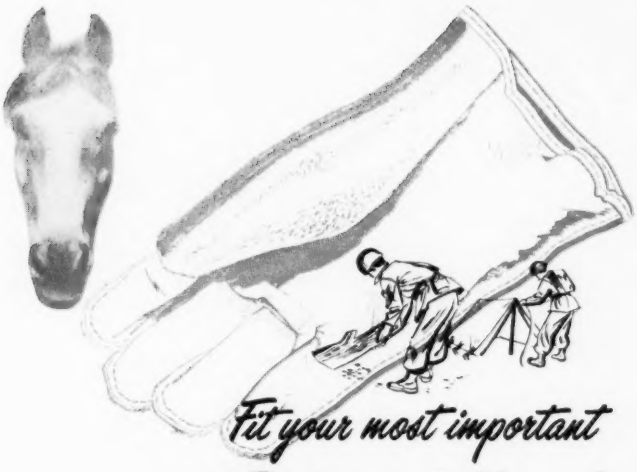

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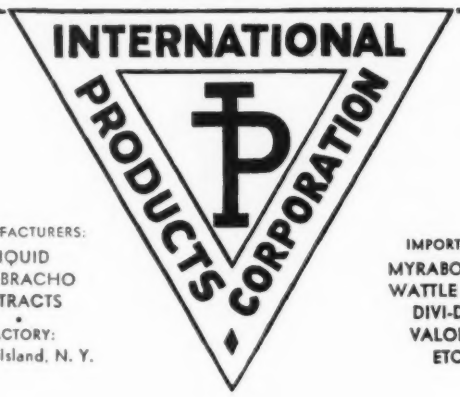

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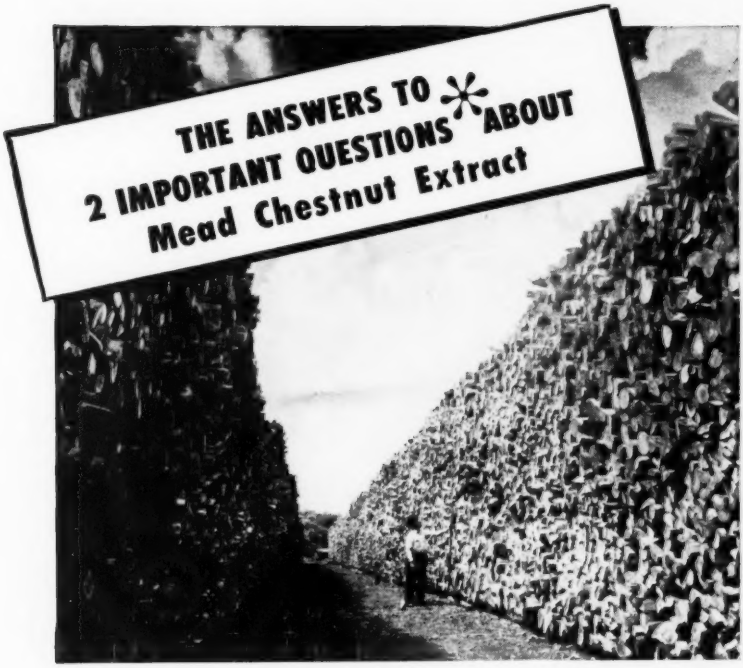

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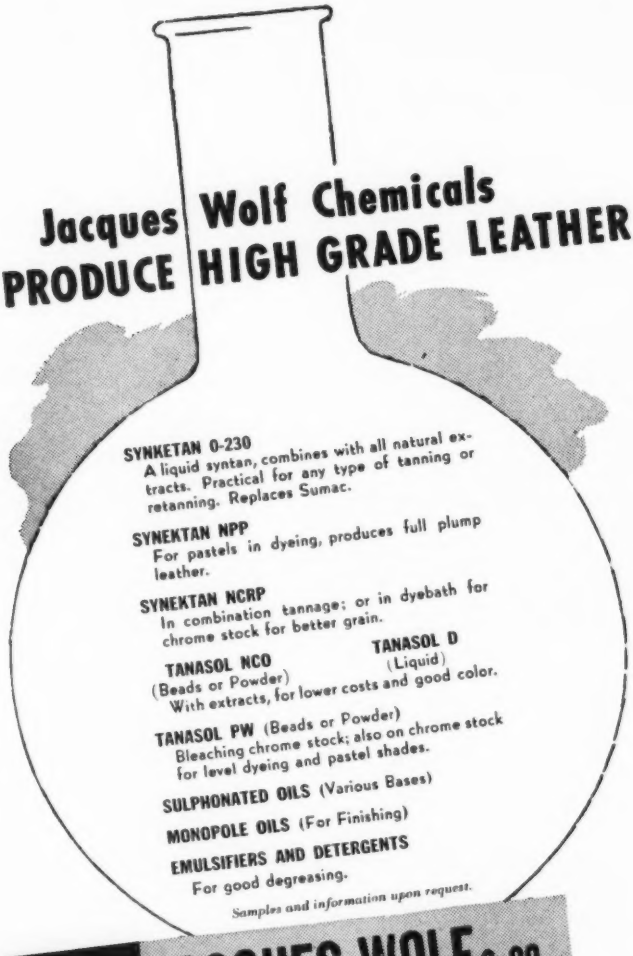

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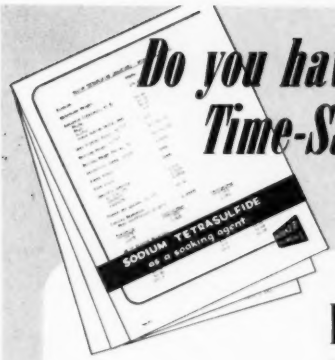

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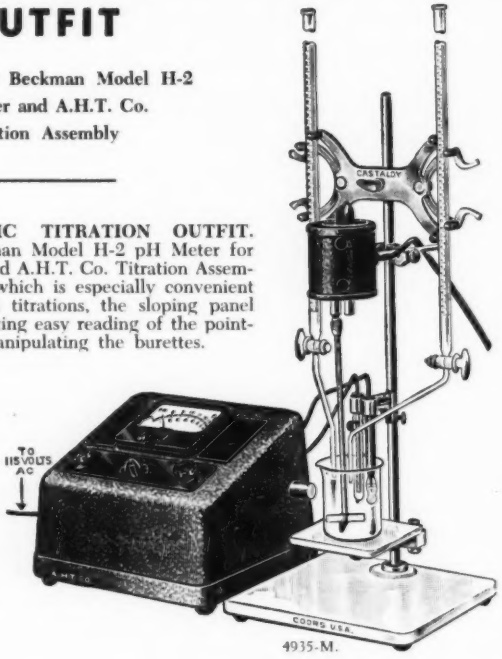

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Statistical Quality Control

I. An Introduction of its Application in the Tanning Industry

By WILLIAM R. COX

Department of Basic Science in Tanning Research
Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati 21, Ohio

The most successful tanner is he who produces the highest proportion of first grade leather. The interest, therefore, should be to determine means of obtaining the highest proportion of first grade leather. One way of doing this is to learn to locate and eliminate the causes of off-grade production. Many other industries have found statistical quality control a great help in this direction.

Fortune Magazine [1] called statistical quality control "One of the sharpest management tools developed in half a century." Developed in 1922 by Shewhart [2] it was not until World War II that quality control methods were generally adopted. Many industrialists at first resisted the introduction of statistical quality control, saying that their particular industry was different. But at the present time, quality control has been found useful in every industry where it has been introduced, and many manufacturers have realized striking reductions in "off-grade" material.

Today, quality control has been successfully adopted by many branches of the chemical industry, but only in isolated instances have tanners investigated any of the methods. The variability of hides and skins has long been accepted as an insurmountable obstacle to the exact control of leather quality. Statistical quality control offers to the tanner a promising means of estimating and detecting the limits of product variability so that he may be able to improve his leather quality.

The purpose of this paper is to introduce briefly some of the simpler methods of statistical quality control. That the methods are applicable to the leather industry will be demonstrated by means of actual tannery processing data. As with any new tool we must be careful at first not to oversell quality control. The mere maintenance of a couple of control charts will not transform the output of a tannery, but when intelligently applied, control charts will supply a sound basis for the detection of some of the common causes of lack of uniformity in leather.

How quality control is applied to detect non-uniformity in an operation or process will be shown later on. First, we shall describe the construction of the basic tool of the quality control engineer—the control chart.

Control Charts

Statistical control begins with the control chart. In its simplest form the control chart is a graphical method for recording process data. Lines called "control limits" are then plotted on the graph. Calculated from the process data these control limits serve to permit decisions regarding the range of uniformity of the process.

For purposes of illustration, we shall construct two simple tannery control charts; first, a control chart for shrinkage temperature, and later, a control chart for pickle pH. The basic information for these charts was obtained from the production records of a chrome side-leather tannery.

TABLE I

Shrinkage Temperature of Chrome Side Leather
(24 hours after tannage)

Note: Each value is the mean of three determinations for each drum.

	Date: October 3rd Shrink Temperature °F.	Date: October 4th Shrink Temperature °F.	
Lowest	*193	201	
	198	197*	Lowest
	194	199	
	198	202	
	200	201	
	196	202	
	196	202	
	201	202	
	200	201	
	195	203	
	196	201	
	198	203	
	200	200	
	197	204	
	201	205	
Highest	*204	201	
	199	207*	Highest
	201	205	
	201	204	
	197	203	
	201	205	
Total	4166	4248	
Mean $\bar{X}$	198.4	202.3	
Highest	204	207	
Lowest	193	197	
Range (R)	11	10	
n	21	21	

Table I shows for two days the average shrink temperature of each individual drum of leather. The shrink temperatures recorded were those obtained

twenty-four hours after tannage. Each value is the average of three determinations. Table I is illustrative of the basic data available in the tannery for the construction of a control chart.

Construction of the Control Chart

The first step in the construction of a control chart is to separate the data into some sort of groups. In the present example we have a ready-made group—a day's production of leather.

Next, we calculate and record the average for each group, (in quality control language $\bar{X}$). In the present example the group averages are the daily average shrink temperatures. We also calculate the daily ranges (R). If we look at Table I we find that for each of the two days, the highest and the lowest individual drum shrink temperatures are marked. The difference between these two values is the range, and has a special significance which will be shown later.

Table II is a record of the group averages and ranges such as would be obtained from data similar to Table I. The data are divided into two sections: the first section covering the operation of the tannery for the month of October, while the second section covers a portion of the following January. Also shown in the table are the grand averages shrink temperature ($\bar{\bar{X}}$) and the average range ($\bar{R}$) for each section of the data.

Except for the calculation of the control limits previously mentioned we now have all the information necessary to construct the control chart. The computation of the control limits is a simple operation. However, in order to have an understanding of the meaning and the use of the control limits some preliminary discussion is required. For a more complete discussion of control chart theory the interested reader is referred to standard works on the subject. [3].

In order to explain the meaning of the control limits we must introduce the idea of distributions of measurements, i. e. to show how a series of individual measurements are spread out around their average value. To obtain an idea of how the shrink temperature measurements are distributed, we have divided each day's values into a number of groups. In one group we have placed all the values which lie between zero and one degree above the individual daily mean shrink temperature. A second group includes those values which are between one and two degrees above the daily means, and so on. A similar series of groups includes all those values below the daily means. Table III shows the frequency of a measurement whose value is any specified amount from the daily means.

Figure I is a plot of the distribution of the data of Table III. The plot is in a form usually called a histogram where the data are presented as a series

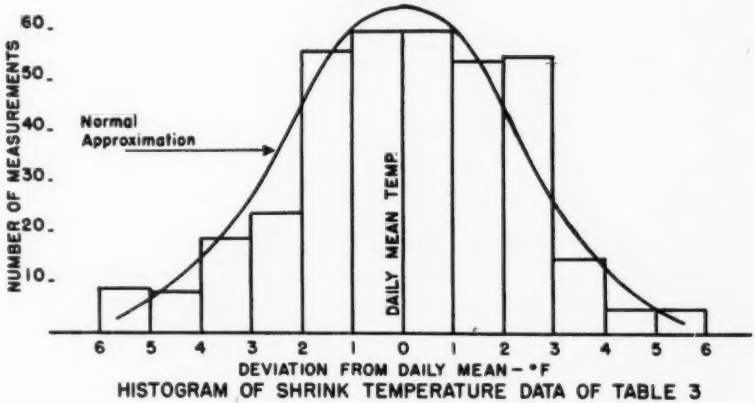
TABLE II

Table Of Daily Average Shrinkage Temperatures and Daily Range of Shrinkage Temperature

Date		No. of Drums	Mean Shrink Temp. °F.	Range °F.
I. First Period		n		
Monday October	3	21	198.4	11
	4	21	202.3	10
	5	19	202.1	6
	6	19	201.4	6
	7	18	203.4	7
Monday October	10	17	200.8	11
	11	17	201.8	11
	12	16	202.1	9
	13	17	202.5	7
	14	17	203.1	7
Monday October	17	17	199.7	10
	18	17	202.2	8
	19	19	202.8	7
	20	19	202.7	7
	21	18	203.9	9
Monday October	24	17	202.4	9
	25	19	204.1	5
	26	19	203.7	9
	27	19	203.9	7
	28	19	204.5	7
Monday October	31	18	204.7	9
	Total		4252.5	172
	$\bar{X}$		202.5	
	$\bar{R}$			8.2
II. Second Period		n	$\bar{X}$	
Monday January	16	19	201.7	10
	17	20	205.0	9
	18	20	205.0	6
	19	20	205.1	10
	20	19	206.8	6
Monday January	23	20	204.4	7
	24	19	207.0	5
	25	19	206.1	7
	26	19	206.1	7
	27	18	207.0	5
Monday January	30	19	202.1	7
	31	20	206.3	4
February	1	19	205.3	6
	2	19	204.3	8
		Totals	2872.2	97
		$\bar{X}$	205.6	
		$\bar{R}$		6.9

of rectangular blocks. The width of the blocks represents the shrink temperature interval covered by each group, while the height of the blocks represents the number of values in each group. Examination of the table and the histogram shows that most of the values lie close to the mean. More important is the fact that few values are found which are very far from the means. In the present case no value more than six degrees above or below the mean was obtained.

FIGURE I



HISTOGRAM OF SHRINK TEMPERATURE DATA OF TABLE 3

TABLE III

Distribution of Shrinkage Temperature Measurements Around Their Daily Mean Shrinkage Temperatures

°F. Mean	No. of Measurements
−5 to −6	9
−4 to −5	8
−3 to −4	19
−2 to −3	24
−1 to −2	56
0 to −1	60
0 to +1	60
+1 to +2	54
+2 to +3	55
+3 to +4	15
+4 to +5	5
+5 to +6	5

This histogram can be approximated by means of a general curve known as the "normal curve of error". A normal approximation to the shrink tem-

perature distribution is represented by the line drawn through the histogram.

The normal approximation represents the data fairly well considering the small number of measurements available. For the purposes of quality control work the data could deviate rather widely from normal and still not vitiate the argument. This is possible because all quality control work deals not with the distribution of the individual measurements but with the distribution of the averages (means) of groups of measurements. Shewhart [4] went to considerable trouble to show that even though the distribution of a series of individual measurements may deviate widely from the normal, the distribution of the averages of groups of the same series of measurements follows the normal law closely. It is because the distribution of averages follows the normal law that quality control is so widely applicable.

What The Normal Law Implies

The statement that the normal law applies to a given set of data implies a number of specific things about the manner in which the data are distributed. When the normal law applies we need know only two things about the data in order to define it completely. The required information is (1) the average (mean value) of the data and, (2) the standard deviation. The first requires no explanation; the second is a measure of the relative spread of the data around the average value. (In Figure I a standard deviation of 2.25°F. was used to draw the normal curve approximating the shrink temperature data.)

Now we borrow a theorem from the theory of probability which states that the standard deviation of the average of a group of values is equal to the standard deviation of the individual values divided by the square root of the number of individuals in the group.

$$\bar{\sigma} = \frac{\sigma}{\sqrt{n}}$$

$\bar{\sigma}$ = Standard deviation of the average
σ = Standard deviation of the individual measurements
n = Number of measurements in the group.

In terms of the shrink temperature measurements where we took in drawing

$$\sigma = 2.25°\text{F.}$$

the normal curve, and where (n) the number of measurements in each group is approximately 18, then

$$\bar{\sigma} = \frac{2.25}{\sqrt{18}} = 0.53°\text{F.} \qquad \text{(approx.)}$$

From this value we may proceed to make some estimates of how the daily average shrink temperatures may be expected to vary.

TABLE IV

Table Showing Distribution of Normally Distributed Values About Their Mid-point in Terms of the Standard Deviation, σ.

Distance Above or Below Mid-point	Per Cent of Total Number of Values Included
σ	68.26
2 σ	95.45
3 σ	99.73

For the normal curve Table IV has been prepared which gives in terms of the standard deviation, the percentage of the total number of measurements whose values are less than any specific amount from the midpoint of the curve.

It is readily seen from the table that only a very small number of values lie beyond the 3 σ limit. In a control chart for daily average shrink temperature a value beyond the 3 σ limit will occur naturally only about three times in four years. Conversely when such a value does occur, we can usually say with a good deal of confidence that something has happened to alter the process. In other words when the average shrink temperature of any one day's production differs by more than 3 x 0.53°F. or 1.6°F. from the grand average ($\bar{X}$) there is a good reason for asking "what happened?" This then is the basis for the control limits on a control chart.

To complete the control chart it is only necessary to erect two control limits equidistant above and below the central line ($\bar{X}$) and at a distance of 3 σ from the central line. Required now is a convenient method for computing the 3σ values. The range (the difference between the largest and the smallest) of the individual drum shrink temperature measurements bears a definite relation to the standard deviation. To facilitate computation, tables have been prepared which permit the direct calculation of the control limits from the average range ($\bar{R}$) and the number of measurements in a group. Such a table is presented in Table V together with the necessary formulas for calculation of the control limits.

In addition to the control chart for average ($\bar{X}$) it is desirable to keep a parallel control chart for range (R). Referring to Table II we see that the range also varies from day to day. A large range means that both high and low values occurred within a day's production. Again, if one drum of leather has an unusually high or unusually low shrink temperature it will be apparent immediately because the range is too large.

Values for calculating control limits for ranges are available and are included in Table V along with the necessary formulas. It should not be forgotten that a point below the lower control limit for ranges is just as much

TABLE V

Factors for Determining From $\bar{R}$ the Three Sigma Control Limits for $\bar{X}$ and R Charts

No. of Observations in Sub-Group	Factor for $\bar{X}$ Chart	Factors for R Chart	
		Lower Control Limit	Upper Control Limit
n	A_2	D_3	D_4
2	1.88	0	3.27
3	1.02	0	2.57
4	0.73	0	2.28
5	0.58	0	2.11
6	0.48	0	2.00
7	0.42	0.08	1.92
8	0.37	0.14	1.86
9	0.34	0.18	1.82
10	0.31	0.22	1.78
11	0.29	0.26	1.74
12	0.27	0.28	1.72
13	0.25	0.31	1.69
14	0.24	0.33	1.67
15	0.22	0.35	1.65
16	0.21	0.36	1.64
17	0.20	0.38	1.62
18	0.19	0.39	1.61
19	0.19	0.40	1.60
20	0.18	0.41	1.59

$U.C.L._{\bar{x}} = \bar{\bar{X}} + A_2\bar{R}$

$L.C.L._{\bar{x}} = \bar{\bar{X}} - A_2\bar{R}$

$U.C.L._R = D_4\bar{R}$

$L.C.L._R = D_3\bar{R}$

Note: By permission from STATISTICAL QUALITY CONTROL, by E. L. Grant. Copyright 1946, McGraw-Hill Book Company, Inc.

"out of control" as a point above the upper control limit. Here the difficulty usually lies with the operator making the determinations. Investigation will frequently show that the measurements were not made properly.

The above explanations now give us all the information required to plot the two control charts which are customarily employed in any quality control work. Let us briefly summarize the steps in the preparation of the control charts.

1. Group the data.
2. Calculate and plot the averages for each group. ($\bar{X}$)
3. Determine the grand average of the groups ($\bar{\bar{X}}$) and the average range ($\bar{R}$). Plot the values as horizontal lines on the control chart.
4. From Table V calculate the control limits for ($\bar{X}$) and R. Plot the control limits as horizontal lines on the appropriate control charts.

5. Give a special mark to any "out of control" points which are above or below the control limit lines.

A qualified quality control engineer will no doubt take exception to the above directions. While they are stripped to a bare minimum it is felt that the instructions are adequate to provide a simple workable control chart.

TABLE VI

Calculation of Control Limits for Shrinkage Temperature

First Period $\bar{\bar{X}} = 202.5°F.$
$\bar{R} = 8.2°F.$
$\bar{n} = 18$

U.C.L.$_{\bar{x}} = \bar{\bar{X}} + A_2\bar{R} = 202.5 + 0.19 \times 8.2 = 202.5 + 1.6 = 204.1°F.$
L.C.L.$_{\bar{x}} = \bar{\bar{X}} - A_2\bar{R} = 202.5 - 1.6 = 200.9°F.$
U.C.L.$_R = D_4\bar{R} = 1.61 \times 8.2 = 13.3°F.$
L.C.L.$_R = D_3\bar{R} = 0.39 \times 8.2 = 3.2°F.$

Second Period $\bar{\bar{X}} = 205.6$
$\bar{R} = 6.9$
$\bar{n} = 19$

U.C.L.$_{\bar{x}} = 205.6 + 0.19 \times 6.9 = 205.6 + 1.3 = 206.9°F.$
L.C.L.$_{\bar{x}} = 205.6 - 1.3 = 204.3°F.$
U.C.L.$_R = 1.6 \times 6.9 = 11°F.$
L.C.L.$_R = 0.40 \times 6.9 = 2.8°F.$

The necessary calculations to complete the control charts for shrink temperature and range are shown in Table VI while Figures II and III are the completed control charts. Before discussing the use of these charts by the tanner we shall prepare a set of control charts for pickle pH. This second set of charts will serve to demonstrate further points in the preparations and use of control charts. All the data for the charts were obtained from the same tannery, and cover the same periods as the control charts for shrink temperature. Sample calculations of $\bar{X}$ and R are shown in Table VII. The complete data are presented in Table VIII along with the calculation of the control limits. Figures IV and V are the completed control charts.

When we look at Figures IV and V it is apparent that something is wrong with the charts. A great many of the points are out of control. If we look a little further we see that the pickle pH values on Monday are so much higher than that of the remainder of the week that they overbalance the rest of the data. When a condition like this takes place the control chart, as drawn,

TABLE VII

Sample Calculations of $\bar{X}$ and R for Pickle pH Control Chart

Date — October 3rd	October 4th	October 5th
*1.90	2.20	2.15
1.90	*2.00	*1.80
2.25	2.00	*2.20
2.30	2.10	2.10
2.45	2.20	2.05
2.25	2.00	2.00
*2.50	2.10	2.10
2.45	2.10	2.05
2.40	2.00	2.05
2.15	2.10	2.10
2.20	2.00	2.05
2.35	2.00	2.10
2.35	2.05	2.10
2.40	2.20	2.20
2.35	2.30	2.05
2.30	2.05	2.20
2.15	*2.35	2.20
2.20	2.15	2.15
2.20	2.00	
2.10	2.10	
2.40	2.00	
Total 47.60	43.90	37.65
Average ($\bar{X}$) 2.27	2.09	2.09
Highest 2.50	2.35	2.20
Lowest 1.90	2.00	1.80
Range (R) 0.60	0.35	0.40
n 21	21	18

is useless. It indicates the lack of uniformity in processing. When such condition is changed then a satisfactory chart can be established and it will serve as a guide in checking the production for quality control.

We know that the high values are out of control, so let us eliminate them and recalculate the charts on the new basis. Table IX and Figures VI and VII show that same data when recalculated with the Monday values eliminated. Figures VI and VII give a much better conception of the remainder

TABLE VIII

Data For Control Chart For Pickle pH

I. First Period

Date		n	$\bar{X}$	R
Monday October	3	21	2.27	0.60
	4	21	2.09	0.35
	5	18	2.09	0.40
	6	19	2.09	0.30
	7	18	2.14	0.30
Monday	10	17	2.47	0.60
	11	17	2.08	0.40
	12	17	2.06	0.25
	13	17	2.18	0.40
	14	17	2.05	0.40
Monday	17	17	2.45	0.50
	18	17	2.07	0.30
	19	19	2.12	0.40
	20	19	2.15	0.30
	21	17	2.18	0.30
Monday	24	17	2.71	0.75
	25	19	2.12	0.25
	26	19	2.20	0.40
	27	19	2.18	0.35
	28	19	2.17	0.40
Monday	31	18	2.60	0.55
		Total	46.47	8.50
		$\bar{\bar{X}}$ =	2.21	
		R =		0.41

Calculation of Control Limits – Control Limits for $\bar{\bar{X}}$

$$U.C.L._{\bar{x}} = \bar{\bar{X}} + A_2\bar{R} = 2.21 + 0.19 \times 0.41 = 2.29$$

$$L.C.L._{\bar{x}} = \bar{\bar{X}} - A_2\bar{R} = 2.21 - 0.19 \times 0.41 = 2.13$$

Control Limits for R

$$U.C.L._R = D_4\bar{R} = 1.61 \times 0.41 = 0.66$$

$$L.C.L._R = D_3\bar{R} = 0.39 \times 0.41 = 0.16$$

of the data. As was done here, it is frequently useful to recalculate the control limits after elimination of the out of control points. The corrected chart will usually yield more information about the process.

TABLE VIII (Continued)

II. Second Period

Date		n	$\bar{X}$	R
Monday January	16	19	2.30	0.65
	17	20	2.08	0.30
	18	20	2.14	0.30
	19	20	2.28	0.60
	20	19	2.27	0.20
Monday	23	20	2.58	0.60
	24	20	2.33	0.55
	25	19	2.32	0.45
	26	19	2.28	0.90
	27	18	2.28	0.45
Monday	30	19	2.35	0.55
	31	20	2.23	0.30
February	1	19	2.18	0.40
	2	19	2.14	0.35
		Total	31.76	6.60
		$\bar{\bar{X}}$ =	2.27	
		$\bar{R}$ =		0.47

Calculation of Control Limits – Control Limits for $\bar{\bar{X}}$

$$U.C.L._{\bar{x}} = \bar{\bar{X}} + A_2\bar{R} = 2.27 + 0.19 \times 0.47 = 2.36$$

$$L.C.L._{\bar{x}} = \bar{\bar{X}} - A_2\bar{R} = 2.27 - 0.19 \times 0.47 = 2.18$$

Control Limits for R

$$U.C.L._R = D_4\bar{R} = 1.60 \times 0.47 = 0.75$$

$$L.C.L._R = D_3\bar{R} = 0.40 \times 0.47 = 0.19$$

Use of the Control Chart by the Tanner

The utility of the control chart to the tanner is perhaps best demonstrated by an examination of the sample control charts which we have prepared. Let us consider the information which is contained in the individual charts in the light of its possible utility.

Control Chart for Shrink Temperature

Several points on the shrink temperature control chart are out of control, that is the points lie above or below the control limits which were set up. Most of the out of control points are values which were obtained for leather

FIGURE 2
CONTROL CHART FOR DAILY MEAN SHRINK TEMPERATURE
($\bar{x}$ CHART)

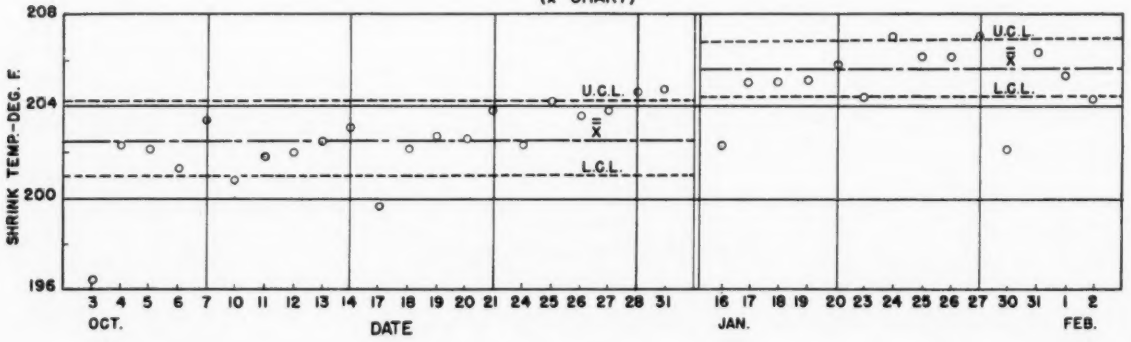


FIGURE 3
CONTROL CHART FOR DAILY RANGE
(R CHART)

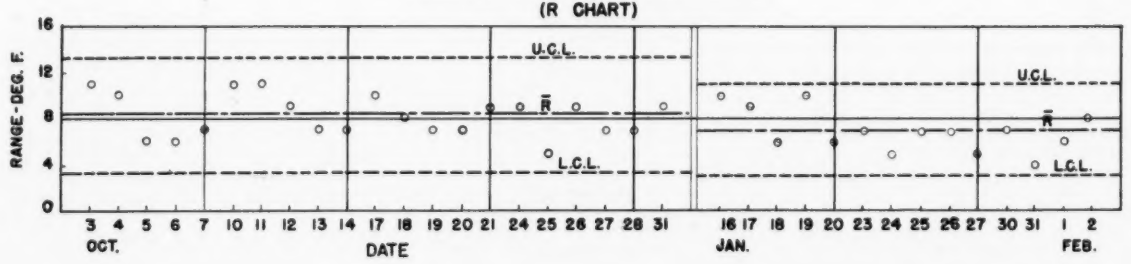


FIGURE 4
PRELIMINARY CONTROL CHART FOR PICKLE pH
($\bar{x}$ CHART)

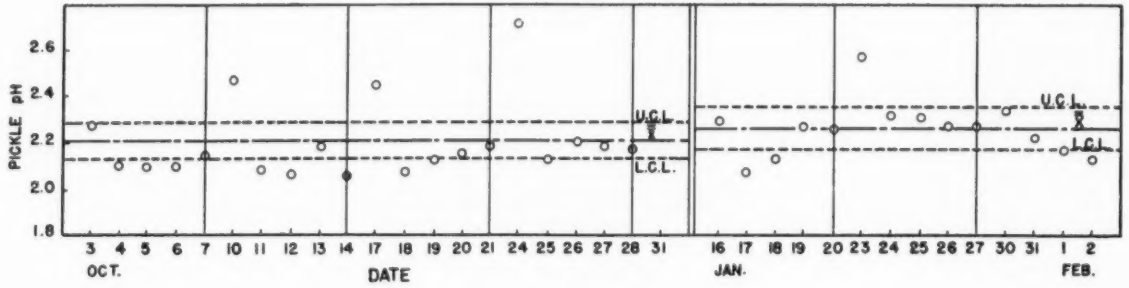


FIGURE 5
CONTROL CHART FOR DAILY RANGE
(R CHART)

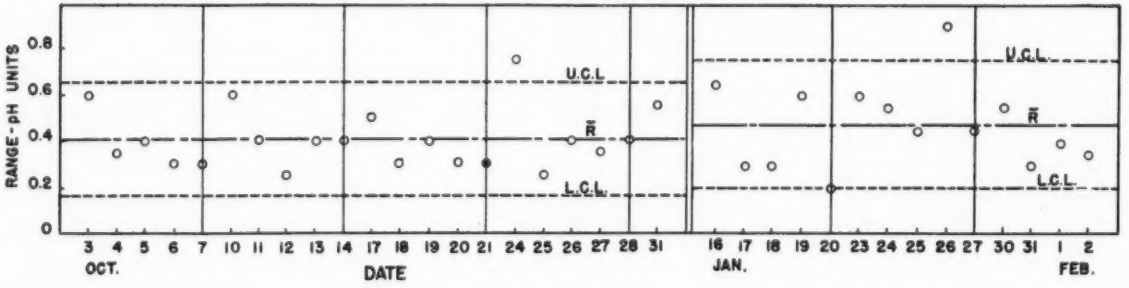


TABLE IX

Recalculation of Pickle pH Data
(Monday data eliminated)

I. First Period

Date		n	$\bar{X}$	R
October	4	21	2.09	0.35
	5	18	2.09	0.40
	6	19	2.09	0.30
	7	18	2.14	0.30
	11	17	2.08	0.40
	12	17	2.06	0.25
	13	17	2.18	0.40
	14	17	2.05	0.40
	18	17	2.07	0.30
	19	19	2.12	0.40
	20	19	2.15	0.30
	21	17	2.18	0.30
	25	19	2.12	0.25
	26	19	2.20	0.40
	27	19	2.18	0.35
	28	19	2.17	0.40
		Total	33.97	5.50
		$\bar{\bar{X}}$ =	2.12	
		$\bar{R}$ =		0.35

U.C.L. $\bar{x}$ = 2.12 + 0.19 x 0.34 = 2.12 + 0.06 = 2.18
L.C.L. $\bar{x}$ = 2.12 − 0.06 = 2.06
U.C.L.$_R$ = 1.61 x 0.34 = 0.55
L.C.L.$_R$ = 0.39 x 0.34 = 0.13

tanned on the first day of the week, namely, Monday. This indicates that the leather tanned on a Monday has a shrink temperature which is somewhat different from that of the leather tanned during the balance of the week. In the particular case under consideration it is known that the tanner was aware of this fact. However, he did not know that the shrink temperature of the Monday leather is itself entirely too variable. If we look at the control chart we see that the spread between the highest and the lowest Monday value is roughly three times the control limits for the rest of the week, which is far beyond normal expectations.

TABLE IX (Continued)

II. Second Period

Date		n	$\bar{X}$	R
January	17	20	2.08	0.30
	18	20	2.14	0.30
	19	20	2.28	0.60
	20	19	2.27	0.20
	24	20	2.33	0.55
	25	19	2.32	0.45
	26	19	2.28	0.90
	27	18	2.28	0.45
	31	20	2.23	0.30
February	1	19	2.18	0.40
	2	19	2.14	0.35
		Total	24.53	4.80
		$\bar{\bar{X}}$ =	2.23	
		$\bar{R}$ =		0.44

$U.C.L._{\bar{x}} = 2.23 + 0.19 \times 0.44 = 2.23 + 0.08 = 2.31$

$L.C.L._{\bar{x}} = 2.23 - 0.08 = 2.15$

$U.C.L._R = 1.60 \times 0.44 = 0.70$

$L.C.L._R = 0.40 \times 0.44 = 0.18$

If variations in shrink temperature show up as variations in the final product, then, twenty per cent of all the leather tanned is out of control and can be expected to be of lesser quality. Usually in a tannery the identity of any particular day's production is lost through sorting into different types and finishes. It would be valuable to trace the Monday leather through the tannery and keep an accurate record of the amount of extra work required to bring the Monday leather into conformity with the balance of the production. If any sizeable proportion of the Monday leather is of lowered quality, economic loss could be the result.

Now, further examination of the control chart will show that during the month of October there was a definite shift toward higher shrink temperatures. A simple way to see that this is true is to compare the number of points above the central line of the chart for the first and second halves of the month. The detection of trends or slow shifts in the production is one of the important uses of control charts. If the trend indicated on the chart is the result of deliberate process changes, all well and good. On the other hand when a process

FIGURE 6
FINAL CONTROL CHART FOR PICKLE pH
($\bar{x}$ CHART)

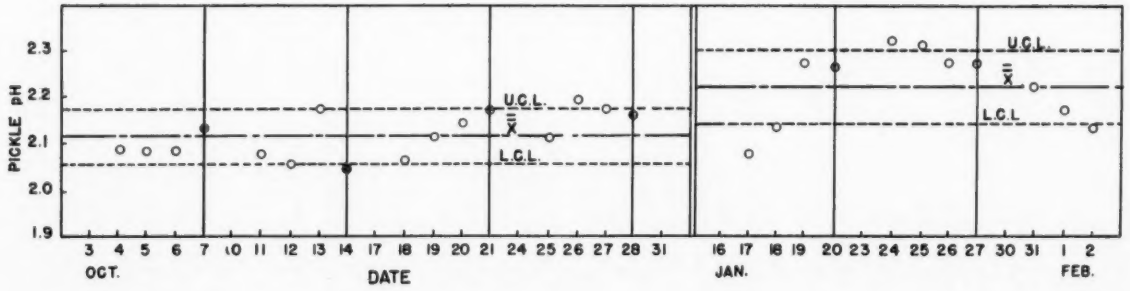
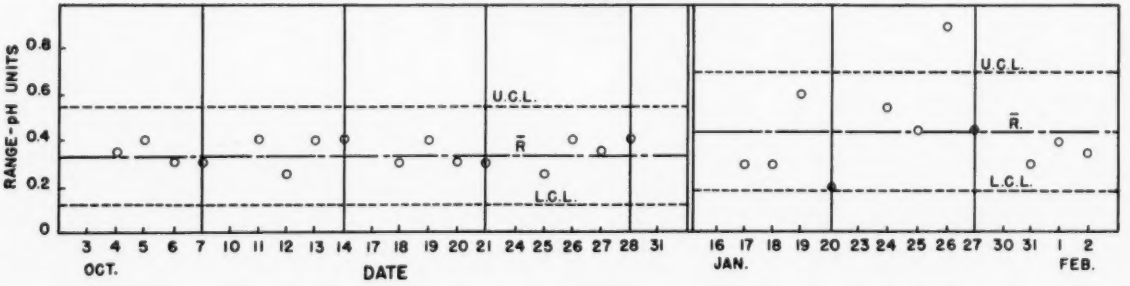


FIGURE 7
CONTROL CHART FOR DAILY RANGE
(R CHART)



starts to shift for no apparent reason, the control chart will permit corrective action to be taken perhaps even before the results of the shift become apparent in the finished leather.

Control Chart for Pickle pH

The wide variability of the Monday leather is even more apparent from the sample control chart for pickle pH. Although there is not sufficient data, there are some indications that a part of the variation in the shrink temperature on Mondays may be a result of the variation in the pickle pH of this stock. With the present process it would be wrong to attempt to bring the Monday pickle pH down to the values for the rest of the week. However, action taken to give a more uniform Monday value may result in better uniformity of the leather tanned.

In addition to the trend toward higher pH values during the month of October, the strong cyclic shift during January is especially important. Here something definitely is wrong. What has happened is the problem for the tanner to solve, but when we have knowledge that there is something wrong we can immediately take steps to correct it.

Control Charts for Range

Disregarding Figure V all but one of the points on the control charts for ranges are within the control limits. This is excellent evidence that each day's production is handled in a uniform manner. If conspicuously less care were employed on certain days it should certainly show up in the range. Whether or not the present range is as low as it should be cannot be determined from the present chart.

The single out of control point (Figure VII, January 26th) is the result of a single low pH value for one drum. Most likely an error was made in recording the pH value. If a control chart had been maintained at the time, the suspected value would have been checked immediately before the sample was discarded.

Conclusion

How far the usefulness of control charts can be extended to aid in producing more uniform leather remains to be demonstrated. However in every other industry where quality control has been given a full and unbiased trial, it has resulted in better control and better quality production. Almost any process variable can be plotted on a control chart and many possibilities will come to mind. For example, a control chart for per cent yield (square feet of leather per pound of hide) would be useful. The extension of such a chart to include a factor for the "sort" (grade of leather) as well, would be but a step.

At best quality control is a tool for the tanner. Properly applied it will often indicate with surprising precision both the time and place of difficulties in production. The really difficult job remains for the tanner; that is the location and the elimination of the causes of the difficulties.

References

1. Fortune Magazine, Vol. XL, No. 5, December 1949.
2. Shewhart, W. A., Economic Control of Quality of Manufactured Product, D. Van Nostrand Co., New York, 1931.
3. Grant, E. L., Statistical Quality Control, McGraw Hill Book Co., Inc., New York, 1946.
4. Shewhart, W. A., loc. cit.

A Conductimetric Study of Chromium Citrate Complex Ions

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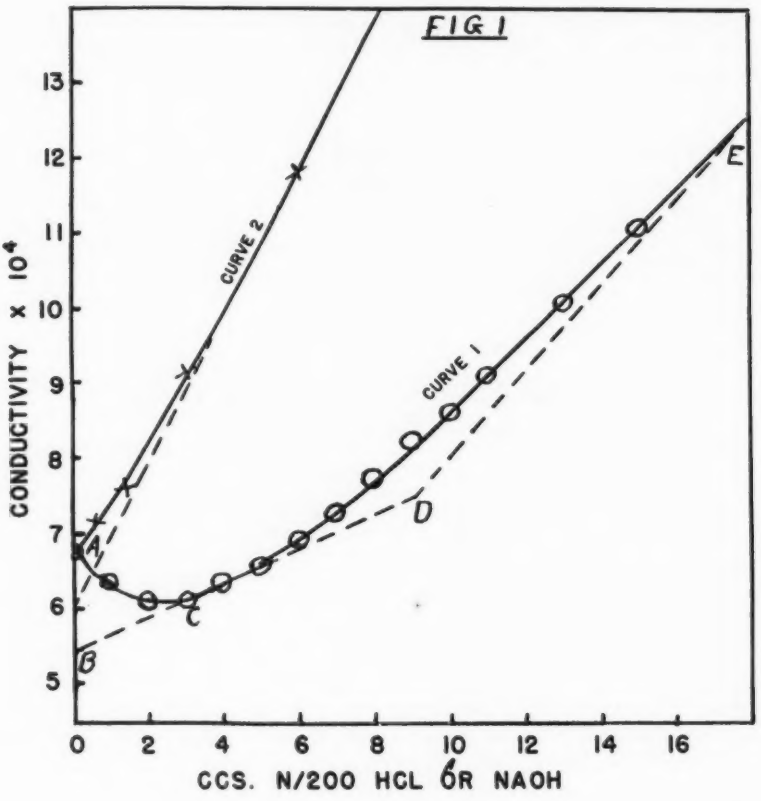
In a previous publication [1] the writer has reported a conductimetric titration study of complex ions formed by boiling one-third basic chromium sulfate with sodium citrate in concentrated solution. It was then shown that the sulfate groups attached to the chromium are displaced, with the formation of new complexes which did not react appreciably with strong acid in cold dilute solution, and titrated only partially with alkali, giving no precipitate towards the endpoint. The present paper records a study of the non-basic complexes formed by boiling both sodium citrate and citric acid with chrome alum, and revises certain conclusions drawn from the earlier work in the light of these new results.

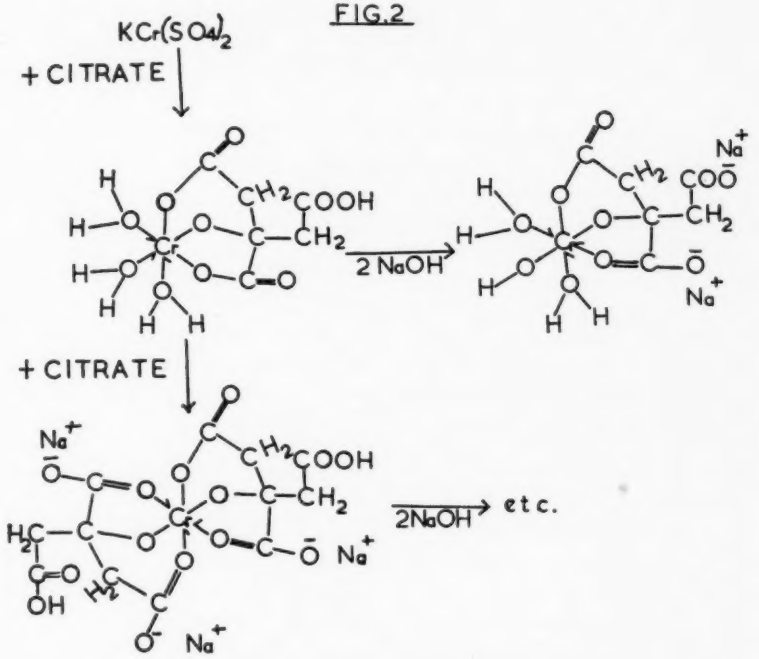
Figure I shows the titration curves of complexes formed by sodium citrate with chrome alum. 3.57 gms. of trisodium citrate were boiled with 5 gms. of chrome alum (1 mole citrate per Cr) in 60 ccs. of water for 1 hour, and one five-hundredth part of this solution titrated in 200 ccs. of water with approximately 0.005 *N* NaOH to give Curve 1, and with approximately 0.005 *N* HCl to give Curve 2. These curves indicate the presence of ionized weak acid in the solution, the ionization being repressed by the addition of excess HCl. The HCl, Curve 2, also indicates that the sodium citrate can no longer be titrated by strong acid. Four explanations appear to be possible:- (a) all three citrate groups have penetrated the complex, involving the formation of double seven-membered rings. Such rings have been shown [2] to occur with maleate complexes and not succinate, and to be relatively unstable. In view



of the stability of the citrate complex and the extent of displacement of sulphuric acid from chrome alum by citric acid, it is considered that this explanation is unlikely. (b) All three citrate groups have penetrated the complex, linking chromium atoms in linear polymers. This is discounted on the grounds of the solubility of the citrate complexes as compared with complexes formed by fumarate, succinate, etc. [2], (c) Two citrate groups have penetrated the complex, while the third has titrated the remaining sulphate, giving a complex containing both an acidic and a basic group. This is considered to be unlikely, as such complexes should tend to link together to form insoluble linear polymers. (d) A double five-plus six-membered internal ring structure is formed involving two of the citrate groups plus the hydroxy group, the H^+ ion generated being taken up by the remaining citrate group

which therefore does not coordinate. This suggestion is considered to be most likely and is illustrated in Fig. 2.

FIG.2



The initial point A of the alkali curve evidently represents an increased conductivity due either to hydrolyzed strong acid or to ionised weak acid, as the alkali curve falls steeply. In order to draw the theoretical alkali titration line, it is necessary to know the mobility of the complex. This is assumed to be of the same order as that of the citrate complex using double the ratio of citrate to chromium (vide infra) viz. 65. The line AB was drawn through the minimum point C with a slope

$$\frac{dK}{dx} = C.V.n.(1_{Na} + 1_{comp})$$

where C = cell constant, V = dilution, n = normality, and 1_{Na}, $1_{comp.}$ etc. are mobilities of the ions, which appear as suffixes. The line DE was drawn through the 50 ccs. titration point with the excess alkali slope

$$\frac{dK}{dx} = C.V.n.(1_{Na} + 1_{OH})$$

The point B is slightly higher than can be accounted for by the formation of an uncharged complex with all sulphates displaced. The end point D corresponds with 75 per cent basicity. It should be noted that, owing to the high slope of DE, an error in the mobility of the complex makes relatively little difference to the calculation of the basicity at the end point D. The structure of this complex and its reaction with alkali are suggested in Fig. 2.

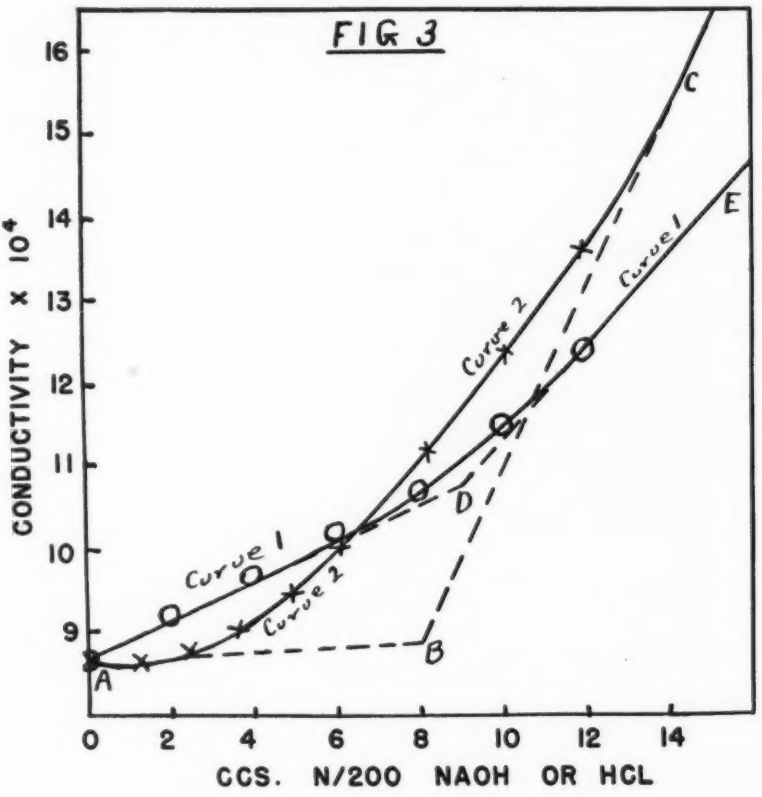


Fig. 3 curves 1 and 2 show the alkali and acid titrations of the complexes formed by boiling chrome alum with double the above quantity of sodium citrate (i. e. 2 moles citrate per Cr). The HCl curve 2 indicates that the majority of the sodium citrate added can no longer be titrated by HCl. In order to obtain a quantitative estimate, the line AB was drawn with the slope

$$\frac{dK}{dx} = \text{C.V.n. } (1_{cl} - 1_{comp})$$

Assuming a complex mobility of 65 (vide infra), the line AB was drawn through A, with a slope equal to C.V.n. 10, while the line BC was drawn through the 50 ccs. excess acid point with the slope

$$\frac{dK}{dx} = \text{C.B.n } (1_{H} + 1_{cl})$$

The end point B indicates that 4 of the 6 citrate groups per Cr_2O_3 cannot be titrated with excess strong acid under these conditions. It should be noted that the slope of BC is so much greater than that of AB, that errors in the assumption of the mobility of the complex ion make relatively little difference to this calculation of free citrate groups.

The initial point A was assumed to have a conductivity proportional to the sum of mobilities of the ions K, 6 Na, 2 $SO_4^{=}$, plus the chromium citrate complex carrying three negative charges. Calculation from the conductivity data gives the ionic mobility of the citrate complex as approximately 65. Using this mobility, the lines AD and DE of Fig. 3 were plotted with the same slopes as BD and DE of Fig. 1 curve 1, giving an end point at 70 per cent basicity. Further curves were plotted using 6, 12 and 24 moles of sodium citrate per Cr_2O_3. In all cases the alkali curves were similar in general form to curve 1 of Fig. 3, and gave end points at 66⅔rds per cent basicity.

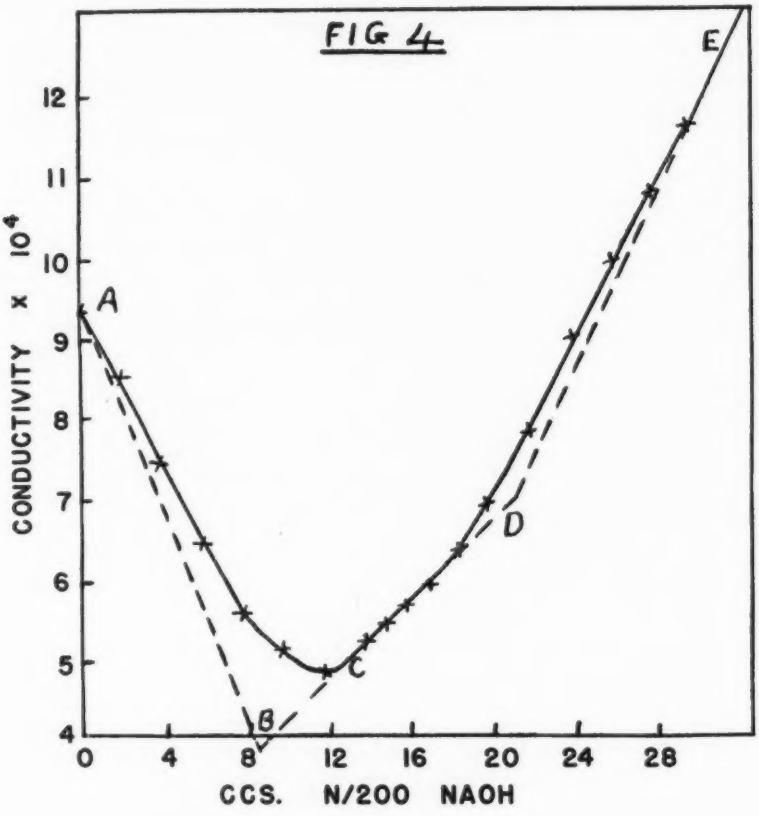
Structural suggestions for these saturated citrate complexes are given in Fig. 2. As in the case of the tartrate complexes [5], the penetration of 3 moles of citrate per chromium in the form of five-membered rings involving the hydroxy group does not appear to take place, because titration with NaOH should titrate three equivalents per Cr, whereas in fact two equivalents per Cr are titrated, suggesting that four acidic anions plus two hydroxy groups are involved in the saturation of the six co-ordination positions of the chromium.

The action of citric acid on chrome alum gave complex ions which titrated as shown in Figs. 4 and 5. Boiling 2.5 gms. of chrome alum in 60 ccs. of water with citric acid in the proportion 1 mole citric acid per Cr, gave a solution which titrated with N/200 NaOH as shown in Fig. 4. The line AB was drawn through A with a slope

$$\frac{dK}{dx} = \text{C.V.n. } (1_{H} - 1_{Na})$$

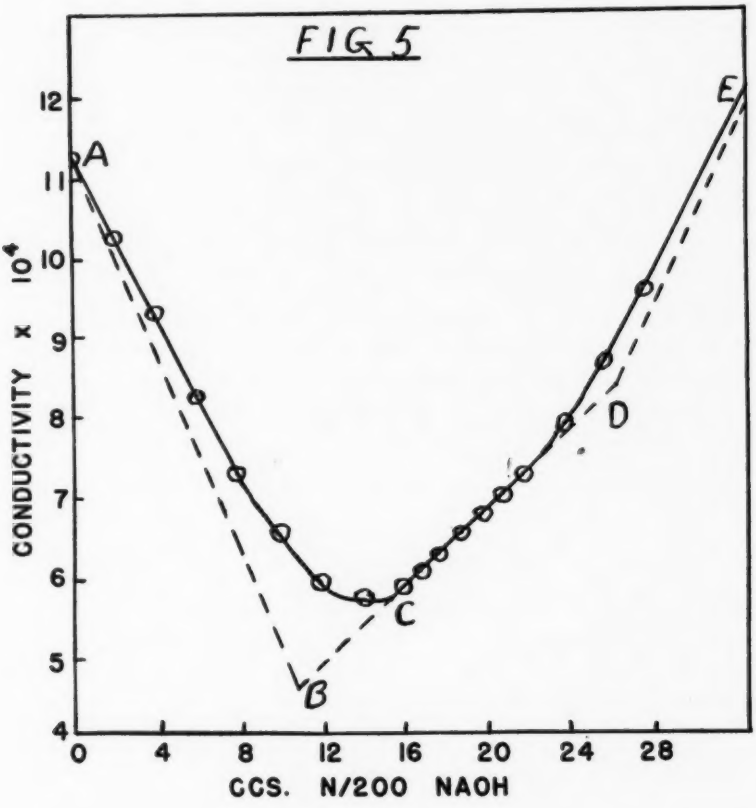
and the line BCD was drawn tangential to curve 1 with a slope

$$\frac{dK}{dx} = \text{C.V.n. } (1_{Na} + 1_{comp})$$



where 1_{comp} was assumed to be 65. The comparatively high slopes of AB and DE are such that errors in the assumptions regarding the mobility of the complex can cause relatively small errors in the estimations of strong acid and basicity at B and D respectively. As in the case of lactic acid [6] and tartaric acid [5], the estimation of strong acid displaced is complicated by the liberation of H ions due to co-ordination of the hydroxy group, and a comparison of curve 1 with the curve obtained using 1 mole per Cr of tartaric acid shows a small difference which can be accounted for by the higher dissociation constant of citric acid. Fig. 4 was repeated using 1.5 moles of citric acid per Cr giving Fig. 5. In general, all that can safely be concluded from these curves is that the degree of penetration of citric acid into the chromium complex is intermediate between that of monobasic acids and the internal

ring-forming diabasic acids, oxalic and malonic, and that tartaric and citric acids give approximately similar degrees of complex penetration.

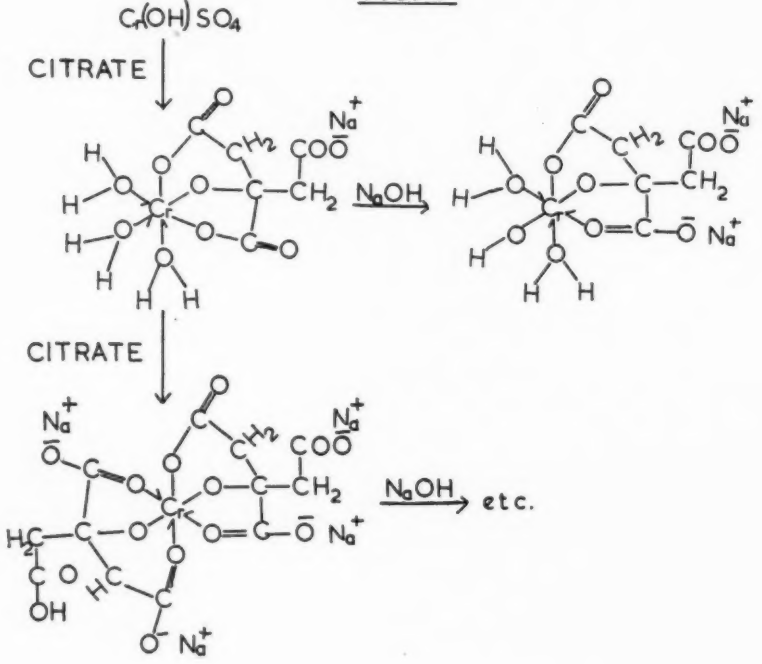


Discussion

The present work on citric acid and the previous papers [5], [6] on tartaric, malic and lactic acids, all appear to support the general rule that ionisation of an acidic OH group must precede stable co-ordination with chromium, so that the hydroxy acids may be expected to penetrate more readily into a basic chromium complex as found by the writer [7] for catechol and pyragallol. In previous work on basic citrate complexes [1] the writer overlooked the possibility of internal ring formation as an explanation of the stability of the

citrate complexes. It was found that this basic citrate complex was resistant to HCl titration even in the proportion 2 moles citrate per Cr, and this must mean the co-ordination of more than two of the six available citrate acid groups per Cr. The earlier structural suggestions are therefore rejected, and the formation of internal rings as in Fig. 2 are suggested instead. It has been shown in the present paper that the complex formed by boiling chrome alum with one mole per Cr of sodium citrate is acidic in character, so that it seems probable that the basic chromium sulphate will be neutralised at the boil with sodium citrate. Evidence in support of this can be found in a paper by Serfass and his co-workers [7], where the effect of sodium citrate on one-third basic chromium sulphate in the ratio 1 mole citrate per Cr reduces the absorption of the chromium complex by a cation absorbent resin from over 90 per cent to less than 10 per cent. A similar effect was observed with tartrate and glycollate, but not with formate and acetate. It is suggested that the absorption by the resin is due to reaction between the resin acid and chromium hydroxide, and that this evidence confirms the suggestion that trisodium citrate may render basic chromium sulphate non-basic. Bearing these factors

FIG. 6



in mind, the suggestions given in Fig. 6 are submitted instead of the structures proposed in the earlier paper [1].

SUMMARY

Conductimetric titration at high dilution of chromium citrate complex ions indicates that trisodium citrate, on boiling with chrome alum in the ratio one mole citrate per Cr, produces a complex which appears to have an acidic group attached. Titration of this with HCl gave no apparent reaction, indicating the disappearance of all three sodium citrate groups. The use of two or more moles of citrate per Cr gave complexes of ionic mobility 65, which appeared to have four co-ordinated citrate acidic groups plus two co-ordinated hydroxy groups per Cr, and all these complexes titrated to approximately two-thirds basicity. The use of citric acid instead of sodium citrate appeared to give a complex penetration similar in extent to that of tartaric acid [5], i. e. intermediate between that of monobasic acids and the more stable ring-forming dibasic acids, oxalic and malonic. This and previous work [5, 6] on hydroxy acids appears to indicate that the neutral hydroxy group ionises on co-ordination and titrates any available sodium salt of available weak acid, so that complex formation is likely to be enhanced by using basic chromium sulphate, the basic group neutralising the liberated acid at the boil. Structural suggestions are given for these citrate complexes formed by chrome alum and one-third basic chromium sulphate.

REFERENCES

1. Shuttleworth: *J.I.S.L.T.C.*, **30**, 342 (1946)
2. Shuttleworth: *J. A. L. C. A.*, **45**, 296 (1950).
3. Shuttleworth: *J. A. L. C. A.*, **45**, 302 (1950).
4. Shuttleworth: *J. A. L. C. A.*, **45**, 169 (1950).
5. Shuttleworth: *J. A. L. C. A.*, **45**, 799 (1950).
6. Shuttleworth: *J. A. L. C. A.*, **45**, 447 (1950).
7. Serfass, Theis, Thorstensen and Argarwal, *J.A.L.C.A.*, **43**, 132 (1948).

Received, January 9, 1950.

A Portable Instrument for the Determination of Bursting Strength and Deformation Resistance of Shoe Soles

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In a previous article we have reported the development of an apparatus to be attached to a tensile test device, and which enables us to determine the

relative resistance of leather to puncture as compared to substitutes. We have also reported an attachment for the determination of deformation resistance of soling materials.

The portable apparatus is simple of operation and inexpensive and with it we can measure the properties of puncture resistance, bursting strength and deformation resistance. The instrument stands but 15 inches high and weighs only 17.5 pounds. It is easy to operate, has the capacity to test the heaviest soling materials and is attractive in appearance.

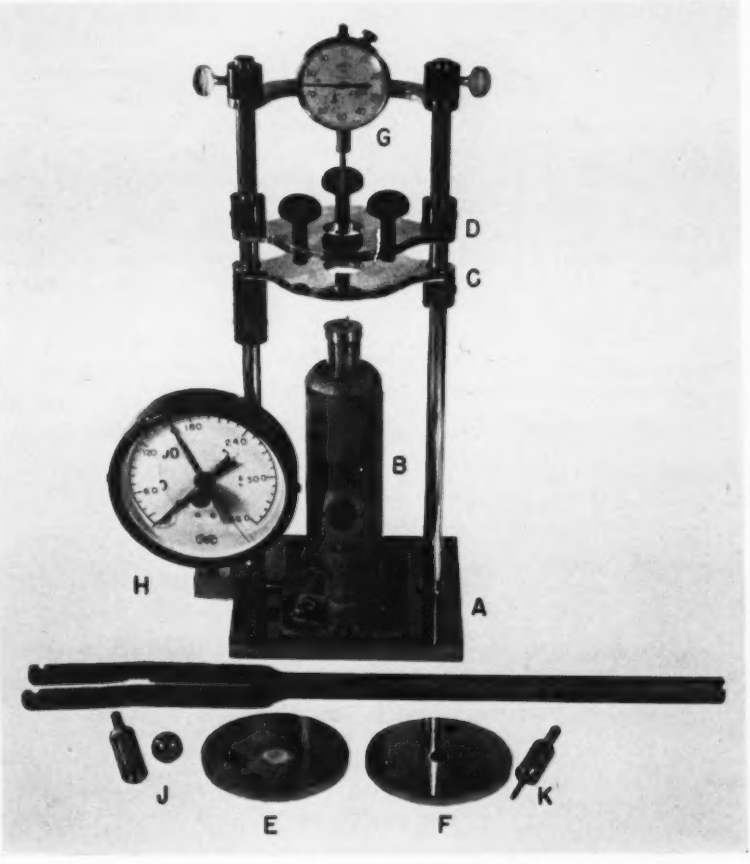

FIGURE I—Portable Apparatus for Bursting Strength and Deformation.

The portable tester is shown in Figure I. The device consists of a heavy base (A) with two .5 inch upright rods on either side of a hydraulic automobile jack (B). Attached to the rods are two horizontal plates (C and D) each with a 1 inch diameter hole in the center directly over the ram of the jack. The upper plate (D) has three thumbscrews located equidistant apart which correspond with the depressions in two other plates (E and F) which have respectively a 1 inch and a $\frac{3}{4}$ inch hole. Above these and made to slide up or down on the rods is a carrier with an Ames dial indicator (G) graduated in 0.001 inch with 1 inch maximum travel. Attached to the jack so that the fluid pressure under the ram is measured directly, is a hydraulic pressure gauge (H). The dial of this gauge is calibrated directly in pounds of force on the ram. In the top of the ram can be placed either a holder for a $\frac{3}{4}$ inch ball bearing (J) or a holder with a $\frac{1}{8}$ inch rod with a spherical end (K).

Bursting Strength or Puncture Resistance

A good correlation has been found by C. W Mann of the Army Quartermaster Department between the results using a $\frac{1}{8}$ inch rod with a spherical tip piercing a specimen held between $\frac{3}{8}$ inch ring clamps and the bursting strength results obtained using the Mullen tester.

To measure bursting strength or puncture resistance of any material with the portable instrument, insert into the top of the ram the holder with the $\frac{1}{8}$ inch spherical tip (K). Place the specimen to be tested between the plates (C and D) and place the plate (F) with the $\frac{3}{8}$ inch hole on top of the specimen. Tighten the thumbscrews making sure they go into the depressions in plate (F). This is to insure centering the plate. Close the bypass valve with the notched end of the jack handle. Check to see that the recording (red) hand of the pressure gauge has been set to zero. Insert the end of the handle into the socket of the jack and pump the jack with slow even strokes until cracks appear in the upper surface of the specimen or the test can continue until the rod pierces completely through the specimen. The maximum force obtained can be read from the position of the red hand on the pressure gauge.

For the purpose of measuring the magnitude of distortion the dial indicator (G) can be slipped down so the foot rests on the surface of the specimen. On this dial the deformation occuring prior to puncture can be followed directly.

To retract the ram of the jack in preparation for another determination, open the bypass valve then insert the forked end of the jack handle as illustrated in Figure II. The handle gives sufficient leverage to relieve the plunger and retract the ram.

For Deformation Resistance

To measure deformation (such as might occur when one steps on a small stone or other uneven surface) with the apparatus use the holder (J) in the

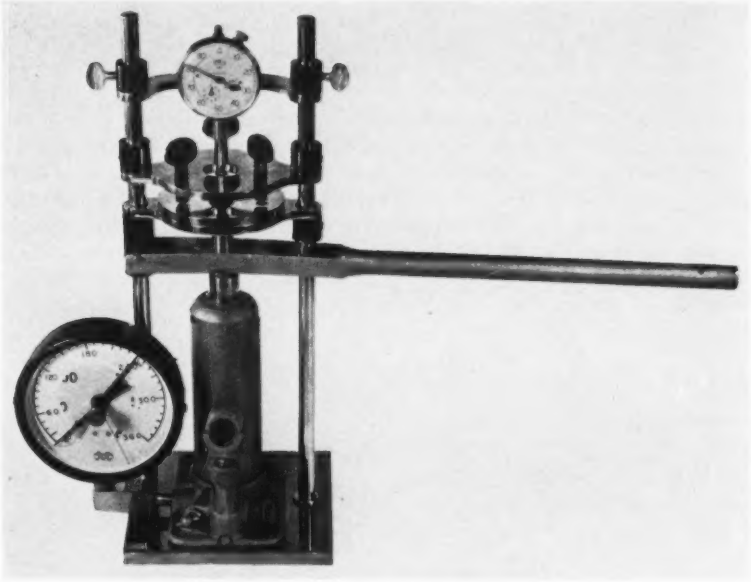

FIGURE II—Arrangement for Retraction of Ram.

head of the ram with the concave end up and in which is placed the $\frac{3}{4}$ inch ball bearing. Place the specimen to be tested between plates (C and D). Place plate (E) with the 1 inch hole centered above the specimen. Tighten the thumbscrews making sure that the screws fit into the depressions of plate (E). Lower the dial indicator so that the foot touches the top surface of the specimen and adjust the indicator to zero. Close the bypass valve with the notched end of the jack handle. Insert the end of the handle into the socket and pump with slow even strokes. Record the readings of the dial indicator against simultaneous readings of the pressure gauge and use the data for subsequent plotting on graph paper, a suggested form is as follows:

Sample	Indicator reading — inches					
	30 lbs.	50 lbs.	70 lbs.	100 lbs.	150 lbs.	200 lbs.
7 iron sole # 1-L	.040	.075	.110	.145	.175	.200
7 iron sole # 1-N	.025	.090	.150	.210	.285	.375

To retract the ram in preparation for another determination open the bypass valve then use the forked end of the handle as indicated in the illustration. An easy downward push will retract the ram.

This simple instrument is capable of doing the same tests as more expensive apparatus, it being portable is easily moved about and its simplicity of operation permits anyone to operate it.

ABSTRACTS

Contributions on Native Vegetable Tanning Materials. VII. Cultivation Experiments with Staghorn Sumac. By W. Grassmann, B. Huber, W. Kuntara, and O. Endisch. *Das Leder*, **1**, 214, 237 (1950). Sumac tannin is one of the oldest and best tanning materials. It penetrates rapidly and makes soft, full, light-colored, light-fast leather. Although used for fine, soft leather, if the supply and price are right it can be used for any kind of leather. In Italy, the home of sumac, a considerable amount is used in combination with chestnut for tanning heavy leather. A review of the literature is given. Experiments on the cultivation of *Rhus typhina* were made in Germany before 1790 but this work was later forgotten. *Rhus coriaria* can be grown only in the warmest parts of Europe because of frost damage but *R. typhina* is winter hardy in Germany. In 1938, experiments with *R. typhina* were started at Tharandt. In the spring of 1940 over 10,000 plants were distributed to more than 30 localities in Germany. At Tharandt, 10 female and 20 male plants, high in tannin, were selected for propagation and study. Leaflets, not leaves, were analyzed and yield data were based on leaflets. Color was measured in a step photometer using Filter S47. There was a seasonal increase in tannin content from 26 per cent in July to 40 per cent in October. Tannin decreased with age of plant. For example, plants containing 36-40 per cent tannin were found to contain only about 24 per cent 4 or 5 years later. There were large differences between different plants. The color of sumac extract is determined by the nature of the plant, the time of harvest, and by oxidative changes which occur during drying and extraction of the leaves. Postmortem changes have been shown elsewhere to be caused by oxidizing or condensing enzymes so their action can be prevented by inactivating them either by a brief steaming of the freshly gathered leaves or by treating the fresh leaves with sulfur dioxide. The average tannin content and extinction coefficient for 5 samples of leaves gathered green and 5 gathered in the fall after turning were as follows: green leaves, not steamed, 22.3 per cent and 0.195; green leaves, steamed, 21.3 per cent and 0.115; colored leaves not steamed, 26.4 per cent and 0.342, colored leaves steamed, 23.7 per cent and 0.196 respectively. Steaming thus lowers tannin content but greatly improves color so it should be used under unfavorable drying conditions or when a very light color is desired. Plants of either high or low tannin content generally maintained this characteristic from year to year when propagated in various locations. Studies on yield were started in 1942. Yield naturally increased with age of the plants. The best yields were obtained in fertilized garden plots. In poor soil tannin content was high but yield was very low. The yield data are poor because there was no close large planting. Yields ranged from less than 100 to 2300 kilograms per hectare, 1000 kilograms being a fair average value. This agrees with reports on yields in Sicily. One can therefore expect 250 kilograms of pure tannin per hectare. Plants that yield well are as important as those of high tannin content. The feared negative correlation between yield and tannin content did not hold true, plants of average yield had the maximum tannin content while those having either a very high or very low yield were low in tannin. The results indicate that thrifty plants of high tannin content (up to 35-40 per cent) can be found. One plant with 48 per cent tannin shows that high tannin content is not, as is often thought, a characteristic of tropical or subtropical plants. Work was

directed to selection of high yielding, high quality varieties. To expedite this work a simple micromethod was required by means of which tannin could be determined in each plant not later than in its second year. Vegetative propagation is possible but one plant will supply root cuttings for less than 100 feet whereas one plant will supply thousands of seed (one kilogram of seed contains about 100,000 seeds). The results in general lead to the conclusion that under the climatic conditions prevailing in Germany, sumac plants can be cultivated that will equal foreign sumac in tanning properties and color but that will be superior in tannin content. I.D.C.

Microdetermination of Free Formaldehyde. By M. Tanenbaum and C. E. Bricker. *Analyt. Chem.* **23,** 355 (1951). Reagents are a 7.5 per cent solution of phenylhydrazine hydrochloride, 5 per cent solution of potassium ferricyanide, 10 per cent solution of sodium hydroxide, and isopropyl alcohol. Analytical procedure is as follows: The sample to be analyzed should not contain over 15 micrograms of HcHo and should not be over 0.6 ml. in volume. Sufficient isopropyl alcohol and water are added to give a total of 1.0 ml. with an isopropyl alcohol content of 40 to 50 per cent. If solid, a weight sufficient to give a formaldehyde concentration of 0 to 15 micrograms is dissolved in 1.0 ml. of 50 per cent isopropyl alcohol. The samples are conveniently handled in 18 x 150 ml. test tubes. To the sample thus prepared, 0.5 ml. of phenylhydrazine hydrochloride solution is added and the solution is allowed to stand 10 $\pm$ 1 minute. Then 0.3 ml. of potassium ferricyanide solution is added and after 5 $\pm$ 0.5 minute, 2.0 ml. of the sodium hydroxide solution are added. After 4 $\pm$ 1 minute, the solutions are diluted to approximately 20 ml. in the test tubes, then transferred to 25 ml. volumetric flasks, and diluted to volume. The optical densities of the solutions are then measured at 520 m μ against a reagent blank of 10 $\pm$ 3 minutes after the initial dilution to 20 ml. The amount of formaldehyde is then found by comparison with a suitably prepared calibration curve.

Kjeldahl Microdigestions in Sealed Tubes at 470°C. By L. M. White and M. C. Long. *Analyt. Chem.* **23,** 363 (1951). Kjeldahl digestions for the microdetermination of hetrocyclic nitrogen can be carried out in heavy walled, sealed glass tubes at 470°C, using concentrated H_2SO_4 and mecuric oxid catalyst. Digestion time is greatly reduced. There is no possibility of nitrogen loss by the method.

Report of the Committee on Oils, Fats and Waxes. XVII. By D. Burton and G. L. Robertshaw. *J. Soc. Lea. Trades Chemists,* **34,** 321 (1950). The committee has taken an active interest in the work of the International Commission for the Study of Fats and the British National Committee for the Soaps and Fats. New and revised British standard specifications have been issued for vegetable oils, technical compound cod oil, cod oil for sulfonation, and an amendment to methods of analysis of oils and fats. The British Standard Methods have been published and include the determination of peroxide value and refractive index in addition to the usual factors. The standard methods have been formulated for degras, sod oil, wool grease, mineral oil and rosin. Recommendations are given covering the cold test for neats foot oil, while a works control procedure for sulfated oils is in preparation.

A Study of the Mold Growth on a Catechol Tanned Leather and of the Associated Changes in Physical Properties. By O. J. Musgrave and R. G. Mitton. *J. Soc. Leather Trades Chemists,* **34,** 324 (1950). Experimental pieces of catechol tanned leather were

given a variety of treatments and then maintained at temperatures and humidity conducive to extensive mold growth. These treatments consisted of application of oil, removal of water solubles and incorporation of a fungicide. Mycological observations were made at intervals, and physical tests carried out on the leather before and after mold growth. The investigation showed that mold growth on catechol tanned leather causes very little change in its physical properties. It was confirmed, however, that molds feed on the water soluble material in leather, and that currying oils play a complicated part in influencing both mold growth and changes in physical properties. During the investigation, several molds new to the leather industry were found. One of these, *Penicillium spiculisporum*, had not previously been isolated in Britain.

The Planning and Interpretation of Experiments on a Variable Material Such as Leather. By R. G. Mitton. *J. Soc. Leather Trades Chemists*, **34,** 343 (1950). A discussion on the application of statistical methods to experimentation in leather science.

The Gains and Losses of Tannins, Acids and Salts in Sole Leather Tannages of Mimosa or Myrobalam. By A. Cheshire and H. Lee. *J. Soc. Leather Trades Chemists*, **34,** 378 (1950). Parallel tanning experiments were conducted with mimosa and myrobalam extracts wherein hide, tannin, salts and acid input were balanced against leather, spent tannin, acid and salts output. Leathers were analyzed and tannin and solids distributed between the leather and the liquors.

The tannin, as determined by the shake method of analysis, is shown in the mimosa and myrobalam feed liquors to constitute 69.8 and 62.4 per cents respectively of the solid material present. Since 91.8 per cent and 91.0 per cent respectively are found in the leather, the yield of tanning matters from these two materials is 132 per cent and 146 per cent. Their value to the tanner is almost exactly equal when the total solids taken out by the leather and not the tannins as determined by the official method are taken as the criterion.

If the tannages were shortened by decreasing the number of pits (10) used in the system, a larger percentage of the solid matter put in would appear in the runaway liquors and the yield of tanning matters found in the leathers would, therefore, decrease. In such event the yield of tanning matter from mimosa extract would be 125 per cent and from the myrobalam extract 138 per cent. These figures are regarded as probably nearer to those obtained in most yards where it is the practice to maintain the strength of the weakest suspender liquor at a tannin figure near to 1 per cent and not the 0.01 and 0.02 per cents obtained in the experiment.

Standards for pH Determinations. By R. E. Smith and R. G. Bates. *J. Soc. Leather Trades Chemists*, **34,** 394 (1950). Three standards to which pH values have been assigned are acid potassium phthalate, a mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate, each at a molarity of 0.025, and 0.01-c borax. The borate is used as the decahydrate and the other salts in their anhydrous forms.

Making Leather with Sound Waves. By T. A. Dickinson. *Lea. and Shoes*, **121,** No. 7, pg. 8 (1951). The suggestion is made that ultrasonics may be used to speed up tanning.

Contact Dermatitis Due to Synthetic Resins in Shoe Linings. By J. W. Jordan. *Lea. and Shoes*, **121**, No. 9, pg. 8 (1951). Forty-seven proven and 29 suspected cases of dermatitis of the feet due to synthetic resins in shoe linings were observed. Patch tests with shoe linings were performed in all 47 cases involved. Thirty-three positive tests were gotten with the lining from one pair of shoes, while in 14 others there were positive reactions to the linings of two or more pairs. Patch tests with fully polymerized, unaltered resins yielded no significant reactions. Ten patients were tested to the ingredients of the resinous lining of one pair of shoes to which a patient who wore them gave a violent patch test, but without significant reactions. Because of the great variety of solvents, plasticizers and chemicals entering into the resinous impregnants of shoe linings, one or more of which may be the irritant, it becomes indeed difficult to trace down the offender. More investigational work is therefore necessary to determine these materials.

Synthetic Resins and Footwear. By A. C. Orthmann. *Lea. and Shoes*, **121**, No. 9, pg. 9 (1951). Insufficient data is provided in Jordan's paper (see above) for the proper appraisal of its conclusions. There is agreement, however, that there has been apparently an increase in dermatitis since synthetic resin impregnated shoe linings have come into general use.

The Advantages and Disadvantages of Masked Chrome Salts in Tanning Box and Velour Leathers. By G. Otto. *Das Leder*, **2**, 1 (1951). Overmasking of chrome liquors has been shown by Stiasny to reduce the chrome content, and fullness of the leather and to reduce its ability to take up dye. Kuntzel found large differences between liquors depending on whether or not they had aged long enough for complexes to form. An aged liquor must contain only a fraction of the masking salt that may be used if the masking salt is added directly to the tanning drum. Glucose reduced chrome tanning liquors vary with the method of preparation. For example, if the sulfuric acid is added slowly a lower temperature is obtained than if it is added rapidly; low temperature favors production of organic acids and greater masking. Masking of cationic liquors reduces take-up of acid dye by the leather; while leather tanned with anionic liquors takes up basic rather than acid dyes. Masked salts give leather with a fine grain but tan slowly so that a 4 day tannage is required. For fine grained leather, tanning may be started in a glucose reduced liquor, then completed in a cationic liquor followed by neutralization with small amounts of salts, such as phthalate or a combination of sulfite and adipate, that will produce full, round leather. Velour leather should be tanned with cationic liquors because it does not require a fine grain but must be full and must dye thoroughly. Prepared chrome tanning materials contain anionic sulfato complexes that form during drying and that return only slowly to cationic hydroxypentaquo compounds when the material is dissolved in water. A drum dried product required over 96 hours to become free from masked chrome salt but a spray dried product only 24 hours. The author has found previously that by repeated tanning and neutralization up to 26.8 per cent Cr_2O_3 can be put into leather. Leathers tanned in five stages were analyzed for Cr_2O_3 and take up of the dye, diamin black BH using 18 per cent of dye on the air dry leather basis. Leather tanned with a glucose reduced liquor contained approximately 5 per cent Cr_2O_3 and took up less than half of the dye whereas leather tanned with an unmasked liquor contained 15 per cent Cr_2O_3 and took up practically all of the dye.

I. D. C.

UV-absorption Measurements on Lignin Tannin and Natural Tannins. By A. W. Sohn. *Das Leder*, **2**, 4 (1951). Freudenberg made measurements in the infrared region on lignin and tannins and in 1945 Hägglund in Stockholm published measurements in the ultraviolet region on ligninsulfonic acid *(I)* and synthetic products similar to lignin. Freudenberg recognized the phenolic character of lignin from which it follows that the tanning principle of lignin is a pyrocatechol component just as is the case for quebracho, mimosa, or other materials of this type. How much nonphenolic material, derived from sugars during the sulfite treatment of the wood, is present in the commercial product is a matter of discussion. Curves, obtained by plotting wave length versus optical density (D), show minima at 260 millimicrons and maxima at 580 millimicrons for *I*. The catechol class of tanning materials, quebracho, mimosa and pine, have curves of the same shape, but D varies with true tannin content. The minimum for quebracho is at a slightly shorter wave length or at about 255 millimicrons. For *I*, D is less than for quebracho at the same concentration, showing qualitatively the difference in astringency and tanning value. Mimosa and pine, at equal concentration, have the same D but different purities, showing that other factors such as molecular size are important. Myrobalans gave a curve resembling that for quebracho except that the minimum was at 245 millimicrons. A different type of curve was found for chestnut and oak. With chestnut extract there was a sharp maximum at 220-230 millimicrons but with oak extract there was only an indication of this maximum. Valonia extract gave a smooth, nonspecific curve. Two mixtures of *I* and quebracho were examined, one containing 2 parts of *I* and 8 parts of quebracho and the other 4 and 6 parts respectively. The maxima in the D curves were between those for the components. The minima for the components, *I* and quebracho, were at about the same level ($D = 0.5$) but for the mixtures the minima were lower ($D = 0.4$). This is not the result of a chemical reaction but of formation of a coordinate valence compound. The curve obtained by plotting D against milligrams of pure tannin is a straight line, so the UV method offers possibilities as a short, rapid method for determining tannin in practical work after standard curves have been obtained with hide powder. I. D. C.

The Use of Beech Sulfite Waste Liquors as Exchange Tannins. By H. Zak. *Österreichische Leder-Zeitung*, **5**, 221, 244 (1950). Utilization of sulfite waste liquors is a problem in all countries. Lignin sulfonate has been used as a mordant in dyeing, as a constituent of impregnating materials, as a medium for growing spirit or food yeasts, in cement mixtures and for making vanillin. The principal components of beech sulfite spent liquors are (1) a free methoxy-containing sugar fraction that is mainly xylose, (2) a cleavable lignin carbohydrate compound, and (3) a sulfonated lignin that can not be split. Oxidative decomposition of the sulfur free lignin fraction gives phenylpropane derivatives and also syringic acid, a dimethyl ether of gallic acid. Similar decomposition of pine sulfite spent liquor yields vanillin. A soft digestion produces a better tanning extract than a hard digestion. Digestion with a liquor containing less than one per cent of calcium results in greater hydrolysis of the carbohydrate lignin sulfonate and a better yield of matter absorbable by hide powder. In an 8 hour digestion pine wood yields an extract containing about 12 per cent solids and beech wood an extract containing over 17 per cent solids. The extract should be free from iron and should have a low content of ash and calcium. Calcium can be removed (1) by the calcium soda process, (2) with soda or ammonium salts or (3) with permutit. Extract quality deteriorates during storage but can be stabilized with sulfonaphthylamine. Hausruck-extract will make serviceable leather when used alone. Analytical values for leathers tanned with a standard mixture, with Hausruck-extract and with a mixture were as follows:

	Standard	Hausruck	Hausruck 50 Standard 50
Ash, %	0.3	0.8	0.2
Combined tannin, %	23.6	17.5	25.1
Degree of tannage	51.0	31.2	54.0
pH	3.7	3.6	3.8
Tensile strength Kg/cm²	277	208	336
Water absorption (24 hour), %	46	45	50

I. D. C.

Sulfite Extraction and its Influence on Tannin Yield and Leather Quality. By J. A. Sagoschen. *Osterreichische Leder-Zeitung*, **6**, 45 (1951). Schweikert *(Ledertech. Rundschau*, 1947 nos. 2 and 3) has stated that the sulfite extraction does not have enough advantages to merit universal adoption. This is contrary to the experience of the author who has worked with the method for 15 years. A questionnaire was sent to 20 firms using the process on pine bark. Only two firms reported any objections to the method; they noted that the leather was a little darker. In general the liquors were clearer and yields of tannin of from 10.7 to 16.7 per cent were obtained instead of from approximately 7 to 10 per cent as were obtained without sulfiting. Yields were thus increased from 16.4 up to 107 per cent. The recommended procedure is to use either a 6 or an 8 stage extraction; to add 0.6 per cent of sodium sulfite to the second best and 0.6 per cent of sodium bisulfite to the third best stage if 6 stages are used or to the third and fourth stages respectively if 8 stages are used. The chemicals should be allowed to react at least 24 hours with the bark; more than 96 hours was of no advantage. The liquors should be pumped, not pressed.

I. D. C.

Hausruck-Extract and its Use. By Karl Blach. *Österreichische Leder-Zeitung*, **4**, No. 24, 8 (1949). Sulfite cellulose waste liquors may provide extracts that have either a tanning or a dissolving action. Beechwood yields a product that is not as good as pine for dissolving insolubles but is much better as a tanning agent. Beechwood extract, sold under the trade name, "Hausruck-extract", will tan leather when used alone, but the leather is of rather poor quality. Tanning, however, is usually done with blends, and Hausruck-extract blends well with other tannins for producing sole or upper leather or for retanning. Hausruck-extract may be obtained either as a powder or liquid (25° Be); it has a brown color; a distinctive odor unlike other sulfite cellulose extracts; it is very hygroscopic and must be stored in a dry place; it penetrates skin rapidly; it is well buffered at pH 3-4; it retards mold growth and it does not give a deep black tint with iron salts. I. D. C.

Beech Sulfite Waste Liquors as a Raw Material for Tanning Extracts. By J. A. Sagoschen. *Das Leder*, **2**, 25 (1951). After much work a satisfactory tanning extract was developed from beechwood waste liquors by the firm Hausruck-Extrakte in Neumarkt i.H. (Austria) in collaboration with H. Zak and the Vienna Research Institute for the Leather Industry. A comparison of the composition of pine and beech liquors is given in the following table: (results are on the dry basis)

	Pine	Beech
Fermentable sugars	20%	1%
Methoxyl sugar	1	4-5
Ligninsulfo acids	40	45
Organic acids	1	1.5
Lignin carbohydrate compounds	25	27

From systematic studies in two factories, the following facts were determined. A better tanning material is made from a "soft cook" than from a "hard cook" (soft or hard refers to the condition of the cellulose after digestion). In the long digestion period of the soft cook, which is required for cellulose for artificial fibers, the incrustations are removed from the cell material and there is extensive hydrolysis of the hemicellulose. The hard cook is a shorter digestion under milder conditions of temperature and pressure, that produces a firm fiber suitable for paper. A liquor of low calcium content gives a better tannin yield than one of high calcium content, when the degree of hardness of the finished fiber is the same, because of greater hydrolysis of the carbohydrate lignin sulfonate. During digestion of pine wood, purity (tannin as percentage of soluble solids) of the liquor increases rapidly to a maximum of 50 in approximately 4 hours, then falls to about 48. With beechwood, liquor purity increases rapidly for one or two hours, then remains constant for 4 hours, finally increasing abruptly to 52 or more. Dry matter in the final liquor was 12.3 per cent for pine and 17.8 per cent for beechwood.

In the Lenzinger process less calcium is used than in other processes, and there is partial splitting of the sulfo groups which increases tanning action. Reducing substances and pentosans amount to around 6 per cent, and α and γ and oxyacids and saponins are present which raise surface tension and thus favor penetration into the hide. In blends, beechwood extracts do not prevent fermentation and acid formation.

The raw liquors cannot be used without purification. Four processes are available. (1). Precipitate the ligninsulfo acid with a large excess of lime then convert to sodium and magnesium salts (the American Maratan extract). (2). Precipitate the secondary ingredients with lime or soda, leaving the ligninsulfo acids in solution. (3). Precipitate the ligninsulfo acids with ammonium carbonate. Iron is not all removed by the alkaline processes so that treatment with ferro and ferricyanide mixture or by ion exchange is required. To prevent deterioration of the purified liquor it must be evaporated or converted to a powder at once. Either a vacuum or pressure evaporator may be used. Small amounts of sulfonaphthylamine derivatives stabilize the purity without influencing tanning value. The composition of Austrian Hausruck-Extracts is shown below.

	Liquid	Solid
Matter absorbed by hide powder	22.5	47.3
Matter not absorbed by hide powder	20.5	45.1
Water	56.8	7.6
Ash	3.7	6.5
Tanning value	42.6	45
Combining value	27.9	32
pH, analytical solution	3.5	3.5
Precipitate by salt, 1/3 saturated	10	12
Precipitate by salt, 2/3 saturated	38	40

Beech extract alone produces rather empty, flat leather that is harder and more brittle than quality leather. Use of 30 per cent Hausruck-Extract in a blend does not lower leather quality and does result in a 10 per cent saving of tannin because of its peptizing action on insolubles of the other materials in the blend.

There were only minor differences between sole leathers (3 months' tannage) tanned with and without Hausruck-Extract as is shown by the following analytical data, calculated to 15 per cent moisture basis.

	no Hausruck	30% Hausruck	100% Hausruck
Ash	1.7	1.9	2.5
Water solubles	15.8	16.2	16.0
Combined tannin	25.3	26.5	22.6
Degree of tannage	62	68	53
pH	4.2	3.8	3.2
Tensile strength kg/cm^2	245	238	216
Stretch	35	22	20
Water absorption, 24 hours	48.0	43.6	45.7

I. D. C.

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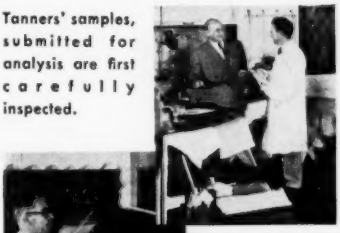

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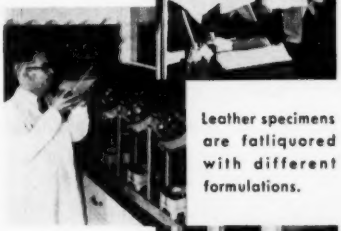

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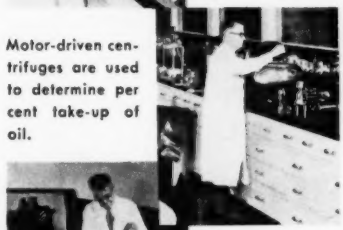

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